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(54) **Process for the production of a spheroidized toner powder.**

(57) A process for the production of a spheroidized toner powder suited for use in single-component toner development of electrostatic charge images is provided, said process comprising the following steps :

(1) dispersing irregularly shaped thermoplastic resin particles containing magnetically attractable material in the presence of colloidal carbon particles having sizes below 100 nanometer in a carrier liquid being a mixture of water and a water-miscible solvent,

(2) heating the dispersion with stirring to a temperature at which said resin particles do not melt but soften and acquire a spherical or substantially spherical shape,

(3) cooling down the dispersion to a temperature at which the resin particles are no longer sticky,

(4) separating the resin particles from the carrier liquid and surplus colloidal carbon by magnetic attraction means, and

(5) drying the separated particles.

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PROCESS FOR THE PRODUCTION OF A SPHEROIDIZED TONER POWER

The present invention relates to a toner composition for use in the developing of electrostatic charge patterns.

In electrostatography a latent electrostatic charge image is made visible, i.e. developed, by charged toner particles.

In electrophotography an electrostatic latent charge image is obtained with an electrophotographic material typically comprising a coating of a photoconductive insulating material on a conductive support. Said coating is given a uniform surface charge in the dark and is then exposed to an image pattern of activating electromagnetic radiation such as light or X-rays. The charge on the photoconductive element is dissipated in the irradiated area to form an electrostatic charge pattern which is then developed with an electroscopic marking material. The marking material or toner, as it is also called, whether carried in an insulating liquid or in the form of a dry powder deposits on the exposed surface in accordance with either the charge pattern or the discharge pattern as desired. If the photoconductive element is of the reusable type, e.g. a selenium coated drum, the toner image is transferred to another surface such as paper and then fixed to provide a copy of the original.

A variety of electrostatic developers are available for use in developing electrostatic charge patterns. According to a known embodiment the developer comprises carrier particles and electroscopic marking or toner particles electrostatically adhering thereto. The carrier particles may comprise various materials and as the name implies, serve as a medium for carrying the electrostatically responsive marking particles to the charge pattern to be developed. Among the more common types of carrier-toner developers are dry developers known for use in magnetic brush development as described e.g. in US-P 3,003,462.

The common magnetic brush development technique involves the use of magnetic means associated with a developing mixture composed of magnetic carrier particles carrying a number of smaller electrostatically adhering toner particles. In this technique the developer composition is maintained during the development cycle in a loose, brushlike orientation by a magnetic field surrounding, for example, a rotatable non-magnetic cylinder having a magnetic means fixedly mounted inside. The magnetic carrier particles are attracted to the cylinder by the described magnetic field, and the toner particles are held to the carrier particles by virtue of their opposite electrostatic polarity. Before and during development, the toner acquires an electrostatic charge of a sign opposite to that of the carrier material due to triboelectric charging derived from their mutual frictional interaction. When this brushlike mass of magnetic carrier with adhering toner particles is drawn across the photoconductive surface bearing the electrostatic image, the toner particles are electrostatically attracted to an oppositely charged latent image and form a visible toner image corresponding to the electrostatic image.

As can be learned from the Journal of Applied Photographic Engineering, Vol. 6, Number 6, Dec. 1980 in the tutorial paper "Recent Development in Electrophotographic Processes, Materials, and Related Fields" by Evan S. Baltazzi single-component magnetic toners have been introduced. These toners offer the important advantage of no toner-replenishment and require no carrier to be replaced. In order to have good transfer properties these mono-component toners have to be slightly electrically conductive.

In order to obtain toners with good flowing properties several techniques have been applied to produce spheroidized toner particles.

Toner powders of which the separate particles are solid and spherical, or substantially spherical, in shape are preferred not only because they have better flow properties but also have a higher mechanical resistance than powders consisting of irregularly shaped particles. Spherical powders can be obtained by spraying a melt or solution of thermoplastic resin, in which colouring material, polarity control agent, electrically conductive material and/or magnetic material are, if so required, dissolved or dispersed. However, this preparing method has the disadvantage that a complex apparatus is required and only a limited choice of thermoplastic resins has the required melt viscosity or solubility to apply these techniques.

A very interesting process for the production of spheroidized toner particles is described in US-P 4,345,015.

According to said process irregularly shaped thermoplastic resin particles or such particles impregnated with additive, and silica particles having sizes below 100 nanometer are dispersed in a carrier liquid in which liquid the resin of said resin particles does not dissolve, so as to form a dispersion containing less than 500 g of said resin particles per liter of carrier liquid and hydrophobic silica particles in a small but sufficient concentration to inhibit coagulation of said resin particles when softened; the dispersion is heated with stirring to a temperature at which said resin particles do not melt but soften and acquire a spherical or substantially spherical shape, and this temperature is maintained until substantially all the resin particles

have become spherical or practically spherical in shape; the dispersion is then cooled down to a temperature at which the resin particles are no longer sticky and, finally, the resin particles are separated from the dispersion liquid, and dried.

It has been described in said US-P document (column 4, lines 40-47) that if a dispersion of irregularly shaped resin particles is heated, whilst stirring in said carrier liquid in which, however, no hydrophobic silica particles are present, the resin particles will coagulate at a temperature lying below the temperature at which the resin particles acquire a spherical shape. This coagulation cannot be avoided by stirring more vigorously.

In the above spheroidation technique the silica has to be hydrophobic to avoid changes in conductivity with relative humidity and to make a good adhering contact with the hydrophobic resins used in the toner particles. The hydrophobization of silica requires a special technique for converting the free hydroxyl groups on its surface, e.g. by etherification with a halogen silane. Although the amount of hydrophobic silica particles to be added to the dispersion is very small and, generally, ranges from 0.2 to 2.0 parts by weight per 100 parts by weight of resin particles it has an influence on the optical density of the powder.

It has been found experimentally by us that the above coagulation of molten toner particles in the absense of colloidal silica yet can be avoided by a special procedure according to the present invention.

It is an object of the present invention to provide a process for the production of substantially spherical highly black hydrophobic magnetic toner particles the electric charging of which is practically independent of relative humidity without the presence of hydrophobic colloidal silica.

It is still another object of the present invention to provide a process for the production of substantially spherical magnetic toner particles that can be used as mono-component toner and can be rapidly and efficiently fixed by flash-fusing and/or infra-red radiation and/or pressure fixing at a relatively low energy level.

Other objects and advantages of the present invention will become clear from the further description.

In accordance with the present invention there is provided a process for the production of a spheroidized toner powder, which process comprises the following steps :

(1) dispersing irregularly shaped thermoplastic resin particles containing magnetically attractable material in the presence of colloidal carbon particles having sizes below 100 nanometer in a carrier liquid being a mixture of water and a water-miscible solvent in which the water is present in such a volume ratio with respect to said solvent that the carrier liquid as a whole is no solvent for the resin of said resin particles, so as to form a dispersion wherein the colloidal carbon black particles are present in a concentration at least 50 % by weight with respect to said resin particles thereby inhibiting coagulation of said resin particles when softened,

(2) heating the dispersion with stirring to a temperature at which said resin particles do not melt but soften and acquire a spherical or substantially spherical shape, and this temperature is maintained until substantially all the resin particles have become spherical or practically spherical in shape and adherently covered with colloidal carbon,

(3) cooling down the dispersion to a temperature at which the resin particles are no longer sticky,

(4) separating the resin particles from the carrier liquid and surplus colloidal carbon by magnetic attraction means, and

(5) drying the separated particles.

The irregularly shaped resin particles, from which the present spheroidized particles are made according to the present invention are obtained in a conventional way by grinding the resin mass containing said magnetically attractable material to form a powder.

The introduction of the magnetically attractable material in the resin mass proceeds preferably by melting the thermoplastic resin and adding the magnetically attractable material thereto in finely divided state, cooling down the resin melt to a solidified mass, and finally grinding that mass to fine particles.

Suitable magnetically attractable materials are e.g. magnetic or magnetizable metals such as iron, cobalt and nickel and various magnetizable oxides, e.g. Fe_2O_3, Fe_3O_4 (magnetite) and CrO_2. Other useful materials are ferrites, e.g. these containing zinc, cadmium, barium and manganese in their structure. Likewise may be used various magnetic alloys, e.g. permalloys and alloys of cobalt such as cobalt-nickel and the like or mixtures of any of these. Good results can be obtained with about 30 % to about 80 % by weight of magnetic material with respect to the resin binder. The average particle size of the magnetic material is preferably in the range of 1 to 0.1 μm (size determined from electron micrographs). Spheroidal magnetite of that particle size is commercially available under the trade name BAYFERROX of Bayer AG - W. Germany.

The organic solvent used in the carrier liquid for carrying out the spheroidization is preferably an organic solvent completely miscible with water, e.g. ethanol, that may have a solvation action on the resin

involved in the toner particle preparation. Solvation results in some solvent association with the resin by penetration of the solvent into the resin particle surface without dissolving the resin particle giving the resin particles an improved adherence with respect to the contacting colloidal carbon black.

Other water-miscible solvents that give useful results are : methanol, isopropanol, methylethyl ketone, acetone, methyl glycol, tetrahydrofuran, dioxane and dimethyl formamide.

According to a preferred embodiment the colloidal carbon is dispersed already in the carrier liquid before the addition of the resin particles having irregular shape, whereupon the temperature of the obtained dispersion is raised to soften the resin particles and this temperature is maintained until the desired quantity of colloidal carbon black has been deposited onto the resin particles having acquired a spherical shape.

The dispersing of the carbon black proceeds preferably with the aid of an anionic dispersing agent.

Preferred colloidal carbon is carbon black having an average particle size of 10 nm to 100 nm. The particle size is calculated from the specific surface area determined by volumetric nitrogen adsorption based on the theory of Brunauer, Emmett and Teller [ref. J. Am. Chem. Soc. 60, 309-319 (1938)].

Examples of carbon black and analogous forms thereof are lamp black, channel black, and furnace black e.g. SPEZIALSCHWARZ IV (trade-name of Degussa Frankfurt/M, W.Germany) and VULCAN XC 72 and CABOT REGAL 400 (trade-names of Cabot Corp. High Street 125, Boston, U.S.A.).

The characteristics of particularly useful carbon blacks are listed in the following table 1.

TABLE 1

	SPEZIALSCHWARZ	CABOT REGAL 400
origin	channel black	furnace black
density	1.8 g x cm^{-3}	1.8 g x cm^{-3}
average grain size	25 nm	25 nm
oil number (g of linseed oil adsorbed by 100 g of pigment	300	70
specific surface (sq.m per g)	120	96
volatile material (% by weight)	12	2.5
pH	3	4.5
colour	brown-black	black

In the preparation of the irregularly shaped toner particles the magnetic or magnetizable material may be used in combination with carbon black to improve the optical density of the toner and/or to control its conductivity.

In that case the carbon black is used, e.g. in an amount of 3 to 10 %, preferably 5 %, by weight calculated on the total weight of toner.

The optimal mixing temperature is determined by experiments and is normally in the range of 80 to 110°C.

After cooling, the solid mass obtained is crushed and ground e.g. in a hammer mill followed by a jet-mill to an average particle size of 1 to 50 µm. The fraction having an average particle size from 3 to 30 µm is e.g. separated by air sifter and used as such for spheroidization according to the present invention.

The toner particles, subject to whether they are charged triboelectrically or deposited by inductive attraction onto an electrostatic charge image, may further contain a polarity control agent or conductivity controlling agent. Conductivity is effectively controlled with carbon black. Polarity is controlled e.g. with

nigrosine dyestuff and nigrosine dyestuff modified with higher fatty acid as described e.g. in United Kingdom Patent Specification 1,253,573 providing negative triboelectric chargeability and chromium complexed azo dyestuffs providing positive triboelectric chargeability.

Resins or resin mixtures suited for use in the toner preparation according to the present invention have preferably a softening point between 50 °C and 130 °C, more preferably between 80 °C and 110 °C. Examples of such resins are polystyrene, copolymers of styrene with allyl alcohol, copolymers of styrene with C_1-C_4-alkyl acrylates and/or methacrylates, polyvinyl chloride, copolymers of vinyl chloride with vinyl acetate, polyacrylate esters, polymethacrylate esters, polyamides and polyester resins and modified polyester resins, e.g. a propoxylated bisphenol A-fumaric acid polyester. The preparation of said modified polester resins is described in United Kingdom Patent Specification 1,373,220 and its use in xerographic toners is described in US-P 4,271,249. Other suitable resins are polymers derived from methyl-1-pentene as the main component and are described in US-P 4,529,680 relating to the production of mono-component magnetic toner suited for use in pressure fixation. The resins used in the toner particles may be mixed with some amount of natural or synthetic wax within the range of compatibility.

The toner prepared according to the present invention is particularly suited for use as single-component magnetic toner having good flowing properties for application in magnetic brush developing techniques.

In order to still further improve the flowing properties of the present the toner, the spheroidized toner particles are mixed with a flow improving means such as microbeads of a fluorinated polymer and/or colloidal silica particles. The flow improving means is used e.g. in an amount of 0.05 to 1 % by weight with respect to the toner.

Colloidal silica has been described for that purpose in the United Kingdom Patent Specification 1,438,110. For example, AEROSIL 300 (trade mark of Degussa, Frankfurt (M) W.Germany for colloidal silica having a specific surface area of 300 sq.m/g is used. The specific surface area can be measured by a method described by Nelsen and Eggertsen in "Determination of Surface Area Adsorption Measurements by Continuous Flow Method", Analytical Chemistry, Vol. 30, No. 8 (1958) 1387-1390.

Suitable fluorinated polymer beads for improving the flowing properties of the toner as well as of the carrier particles are described in the United States Patent Specification 4,187,329. A preferred fluorinated polymer for said use is poly(tetrafluoroethylene) having a particle size of 3 to 4 um and melting point of 325-329°C. Such poly(tetrafluoroethylene) is sold under the trade name HOSTAFLON TF-VP-9202 by Farbwerke Hoechst A.G. W. Germany.

An other fluorinated polymer useful for that purpose is polyvinylidene fluoride having an average particle size of 5 um sold under the trade name KYNAR RESIN 301 by Pennwalt Corp. - Plastic div. England.

The colloidal silica and at least one of said fluorinated polymers are preferably mixed with the toner in a proportion of 0.15% to 0.075 % by weight respectively. The toner obtains thereby a reduced tendency to form a film on the xerographic plates or drums that have e.g. a vapour-deposited coating of a photoconductive Se-As alloy on a conductive substrate e.g. aluminium.

The following example illustrates the present invention without, however, limiting it thereto. All parts, ratios and percentages are by weight unless otherwise stated.

EXAMPLE

- Particle preparation for spheroidization.

In a laboratory kneading machine were homogenously mixed :

	Parts
Propoxylated bisphenol A fumarate polyester (melting point 120 °C)	50
spheroidal magnetite (average particle size : 0.2 µm)	50

During a 30 min kneading a temperature of 130 °C was maintained.

After cooling the solidified mass was ground in a hammer mill to obtain coarse particles sizing about 500 µm, whereupon a more fine grind was obtained in a jet mill yielding irregularly shaped magnetic

particles of an average diameter of 23 um.

- Spheroidization

A) Preparation of carbon black dispersion.

150 g of CABOT REGAL 400 (registered trade name), 300 g of distilled water and 15 g of a condensation product of formaldehyde with naphthalene sulphonic acid monosodium salt acting as dispersing agent were put into a ball-mill of 1 l containing 600 g of ceramic balls and ground therewith for 92 h.

B) Coating of the magnetic particles with carbon black.

To 788 g of the above prepared carbon black dispersion 740 ml of distilled water and 416 ml of ethanol were added. While stirring to said dispersion 250 g of the above prepared irregularly shaped magnetic particles were added and the whole compostion subjected while fairly mild stirring to a heating procedure as follows :

In 15 min the temperature is raised from 20 to 55 °C.
For 15 min the temperature is maintained at 55 °C.
In 5 min the temperature is raised from 55 to 65 °C.
For 13 min the temperature is maintained at 65 °C.
In 2 min the temperature is decreased from 65 °C to 20 °C.

The thus obtained spheroidized particles are separated from residual carbon black and solvent by cascading the obtained dispersion over an inclined plate having strong permanent magnets underneath. The layer of magnetic particles adhering to said plate is thoroughly washed with running water while maintaining the magnetic attraction force.

After removing the magnets from the plate the no longer magnetically attracted carbon-coated magnetic particles are collected, dispersed again in a liquid mixture of water and ethanol (3/1 volume ratio) and subjected to a heating procedure as follows :

In 18 min the temperature is raised from 20 to 58 °C.
For 15 min the temperature is maintained at 58 °C.
In 2 min the temperature is decreased from 58 °C to 20 °C.

Magnetic separation and washing is repeated, whereupon the carbon-coated magnetic particles are dried in a ventilated drying stove at 40 °C for 48 h.

The thus obtained particles were used succesfully as single-component magnetic toner in magnetic brush development.

Claims

1. A process for the production of a spheroidized toner powder, which process comprises the following steps :

(1) dispersing irregularly shaped thermoplastic resin particles containing magnetically attractable material in the presence of colloidal carbon particles having sizes below 100 nanometer in a carrier liquid being a mixture of water and a water-miscible solvent in which the water is present in such a volume ratio with respect to said solvent that the carrier liquid as a whole is no solvent for the resin of said resin particles, so as to form a dispersion wherein the colloidal carbon black particles are present in a concentration at least 50 % by weight with respect to said resin particles thereby inhibiting coagulation of said resin particles when softened,

(2) heating the dispersion with stirring to a temperature at which said resin particles do not melt but soften and acquire a spherical or substantially spherical shape, and this temperature is maintained until substantially all the resin particles have become spherical or practically spherical in shape and adherently covered with colloidal carbon,

(3) cooling down the dispersion to a temperature at which the resin particles are no longer sticky,

(4) separating the resin particles from the carrier liquid and surplus colloidal carbon by magnetic attraction means, and

(5) drying the separated particles.

2. A process according to claim 1, wherein the magnetically attractable material is spheroidal magnetite having a particle size in the range of 0.1 to 1 μm.

3. A process according to claim 1 or 2, wherein the water-miscible solvent is ethanol.

4. A process according to any of the preceding claims , wherein the thermoplastic resin is composed of a resin or mixture of resins having a softening point between 50 °C and 130 °C.

5. A process according to any of the preceding claims , wherein the magnetically attractable material is present in said particles in combination with carbon black.

6. Process according to any of the preceding claims, wherein said particles before step (2) have an average particle size from 3 to 30 um.

7. Process according to any of the preceding claims, wherein the colloidal carbon particles are dispersed already in the carrier liquid before the addition of the resin particles having irregular shape.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 20 0287

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
Y	FR-A-2 317 687 (OCE- VAN DER GRINTEN) * Claims 5-10; page 5, line 37 - page 6, line 9; page 7, line 2 - page 10, line 24; example * & US-A-4 345 015 (Cat. D,Y)	1-7	G 03 G 9/08

Y	US-A-3 166 510 (C.P. WEST) * Column 1, line 61 - column 3, line 23; column 4, lines 18-40; claims 10,11 *	1-7	

			TECHNICAL FIELDS SEARCHED (Int Cl.4)
			G 03 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-09-1987	VANHECKE H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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